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Review of New Source Performance Standards for Nitric Acid Plants

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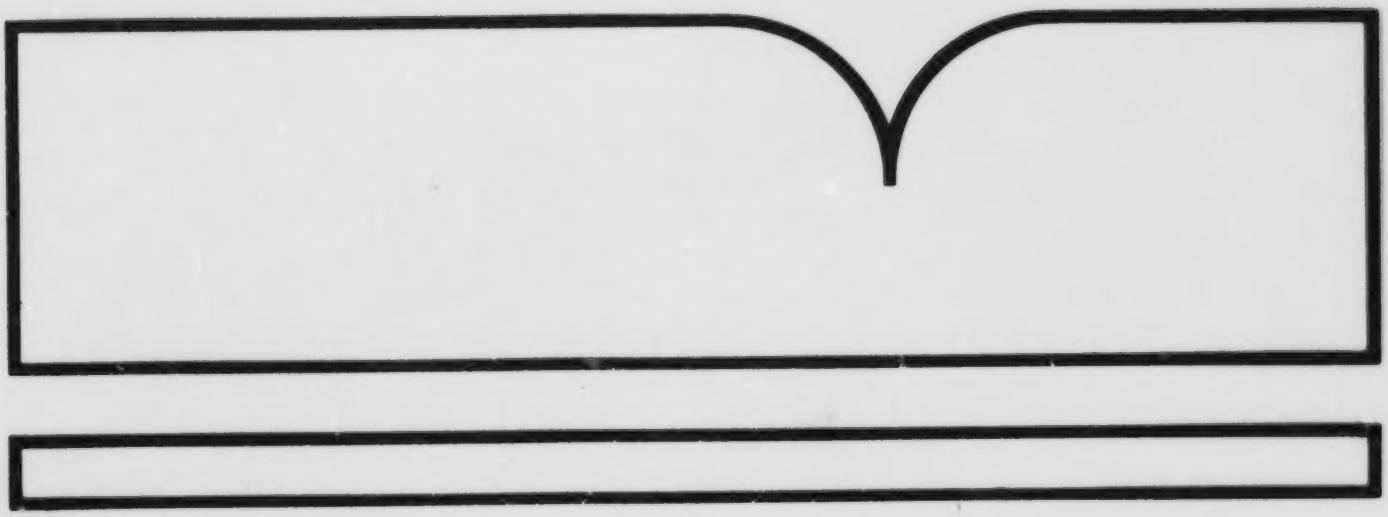

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Review of New Source Performance Standards for Nitric Acid Plants

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This report reviews the current New Source Performance Standards for Nitric Acid Plants. It includes a summary of the current standards, the status of current applicable control technology, and the ability of plants to meet the current standards.

17. KEY WORDS AND DOCUMENT ANALYSIS

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Review of New Source Performance Standards for Nitric Acid Plants

Emissions Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

April 1984

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1. EXECUTIVE SUMMARY

The new source performance standards (NSPS) for nitric acid plants were promulgated by the Environmental Protection Agency (EPA) on December 23, 1971. The standards affect nitric acid production units which commenced construction or modification after August 17, 1971. A nitric acid production unit is any facility producing weak nitric acid (30 to 70 percent in strength) by either the pressure or atmospheric pressure process. The NSPS limits emissions of nitrogen oxides (NO_x).

A review of the nitric acid plant standard was previously conducted in 1979; however, no revisions to the NSPS were made as a result of the 1979 review.

The objective of this report is to again review the NSPS for nitric acid plants. The following paragraphs summarize the findings of this second review.

1.1 BEST DEMONSTRATED CONTROL TECHNOLOGY

The control methods used by nitric acid units subject to the NSPS are extended absorption, catalytic reduction, and chilled absorption with caustic scrubbing. Catalytic reduction was used as the basis for the NSPS since, at the time of the NSPS development, no other NO_x control methods had been demonstrated to achieve the NSPS. Since promulgation of the NSPS, the catalytic reduction process has been largely supplanted by the extended absorption process as the control method of choice for achieving the NSPS due to increasing fuel costs. None of the units built since 1977 are designed with catalytic reduction. The capability of extended absorption and chilled absorption with caustic scrubbing in achieving the NSPS was indicated by information and data obtained during the 1979 review.

Compliance test results for the 10 facilities subject to the NSPS which have started operation since the 1979 review indicated that all have achieved the NSPS with the exception of one extended absorption

unit. This unit has never been operated except for a 2-day startup period during which time the unit was compliance tested and shut down. It is installed as a standby unit for ammunition production.

1.2 ECONOMIC CONSIDERATIONS AFFECTING THE NSPS

The cost effectiveness of achieving the NSPS was estimated for the two most prevalent control systems, extended absorption and catalytic reduction, on nitric acid plant sizes of 181,454 and 907 Mg/D (200, 500, and 1,000 TPD). The cost effectiveness of extended absorption ranges from a cost savings of $46 per megagram for a 970 Mg/D plant ($42 per ton for a 1,000 TPD plant) to a cost of $258 per megagram for a 181 Mg/D plant ($235 per ton for a 200 TPD plant). For catalytic reduction, the cost effectiveness ranges from $841 per megagram for a 970 Mg/D plant ($760 per ton for a 1,000 TPD plant) to $1,153 per megagram for a 181 Mg/D plant ($1,050 per ton for a 200 TPD plant).

Since the NSPS was proposed, 29 nitric acid units have started operation. The growth rate in terms of nitric acid production average 1.7 percent per year between 1971 and 1982. The actual average rate of start-up between 1971 and 1982 has been between two and three units per year.

1.3 STRONG NITRIC ACID PLANTS

The NSPS does not apply to the various processes used to produce strong acid. The rationale for excluding strong acid plants from the NSPS at the time it was developed was that emissions from these strong acid plants are small, about the level of the NSPS, and only one strong acid process was in operation. This review has found two strong acid units which have started operation since 1971, and the reported NO_x emissions from these strong acid plants are below the level of the NSPS.

2. THE NITRIC ACID MANUFACTURING INDUSTRY

2.1 INTRODUCTION

The United States Environmental Protection Agency (EPA) proposed new source performance standards (NSPS) for nitric acid plants under Section 111 of the Clean Air Act on August 17, 1971 (36 FR 15704). These regulations were promulgated on December 23, 1971 (36 FR 24875). The regulation applied to any nitric acid production facility producing weak nitric acid, the construction or modification of which commenced after August 17, 1971.

The Clean Air Act Amendments of 1977 require that the Administrator of the EPA review and, if appropriate, revise established standards of performance for new stationary sources at least every 4 years. The NSPS was previously reviewed in 1979; no changes in the NSPS were made as a result of the 1979 review. The purpose of this report is to review and assess the need for revision of the existing standards of nitric acid plants based on developments that have occurred since the last review or are expected to occur within the nitric acid manufacturing industry. The information presented in this report was obtained from reference literature, discussions with industry representatives, control equipment vendors, EPA regional offices, and State agencies.

2.2 BACKGROUND INFORMATION[1]

Nitric acid is manufactured in the U.S. by the high temperature catalytic oxidation of ammonia. The essential components of an ammonia oxidation nitric acid plant are:

1. Converter or oxidation section where the ammonia vapor and air are mixed and reacted catalytically to oxidize the ammonia.

2. Cooler-Condenser section where the nitrogen dioxide is produced by cooling the reaction gases and weak nitric acid is formed.

3. Absorber section where the cool nitrogen dioxide is absorbed in water to form nitric acid.

In the first step of this process, one volume of anhydrous ammonia is mixed with nine volumes of preheated air and passed through a multi-layered, silk fine platinum-rhodium gauze catalyst at 750° to 800°C (1,380° to 1,470°F). Under these conditions, the oxidation of ammonia to nitric oxide proceeds in an exothermic reaction with a 95 percent yield:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \quad (1)$$

The second step involves the oxidation of the nitric oxide to nitrogen dioxide and its liquid dimer, nitrogen tetroxide:

$$2NO + O_2 \rightarrow 2NO_2 \rightarrow N_2O_4 \quad (2)$$

The forward rate of reaction (2), which is rather slow compared with reaction (1), is favored at lower temperatures and higher pressures. Hence, reaction (2) is always carried out after cooling the gas to 38°C (100°F) or less and, depending on the process design, at pressures up to 500 kilopascals (kPa) (73 psig).

In the final step, the nitrogen dioxide/dimer mixture is cooled further and passed to an absorber where it reacts with water to produce an aqueous solution of 50 to 60 percent nitric acid, the concentration depending on the temperature, pressure, number of absorption stages, and concentration of the nitrogen dioxide entering the absorber:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \quad (3)$$

This reaction is also favored by low temperature and high pressure, because the gases involved are more soluble at lower temperatures and absorption results in a reduction in volume. In fact, some processes utilize the low temperature/high pressure conditions to increase yields.

The formation of nitric acid in Equation (3) involves the disproportionation of nitrogen dioxide to form two moles of nitric acid for every mole of nitric oxide. In order to reoxidize the nitric oxide during absorption, secondary air (also known as bleacher air) is introduced into the absorber along with the nitrogen dioxide. However, the reaction to form nitric acid is never quite complete--the overall process is 95 percent efficient, so that a small quantity of nitrogen oxides, NO_x (NO_2 and NO), is inevitably present in the waste gas discharged from the absorption column. The NO_x in these waste gases is the target for air pollution regulations and control.

Acid product is withdrawn from the bottom of the tower in concentrations of 55 to 65 percent. The air entering the bottom of the tower serves to strip NO_2 from the product and to supply oxygen for reoxidizing the NO formed in making nitric acid (Equation 3).

The oxidation and absorption operations can be carried out at low pressures [100 kPa (14.5 psi)], medium pressures [400 to 800 kPa (58 to 116 psi)], or high pressures [1,000 to 1,200 kPa (145 to 174 psi)]. Both operations may be at the same pressure or different pressures.

Before corrosion-resistant materials were developed (precluding the use of high pressures) the ammonia oxidation and absorption operations were carried out at essentially atmospheric pressure. The advantages over higher pressure processes were longer catalyst life (about 6 months) and increased efficiency of ammonia combustion. However, because of the low absorption and NO oxidation rates, much more absorption volume was required, and several large towers were placed in series.

Combination pressure plants carry out the ammonia oxidation process at low or medium pressure and the absorption step at medium or high pressure. The increased pressure for the oxidation reaction shortens the catalyst's lifetime (1 to 2 months) and lowers the ammonia oxidation conversion efficiency. Thus, lower pressures in the oxidation process are preferred. On the other hand, higher pressures in the absorption tower increase the absorption efficiency and reduce NO_x levels in the tail gas. The advantages of higher absorber pressures must be weighed against the cost of pressure vessels and compressors.

The choice of which combination of pressures to use is very site specific and is governed by the economic tradeoffs such as costs of raw materials, energy and equipment, and process efficiency. In the 1960's, combination low pressure oxidation/medium pressure absorption and single pressure [400 to 800 kPa (58 to 116 psi)] plants were preferred. Since the 1970's, the trend has been toward medium pressure oxidation/high pressure absorption plants in Europe and single pressure [400 to 800 kPa (58 to 116 psi)] plants in the U.S.

The two types of weak nitric acid production processes in use in new U.S. plants, i.e., single pressure and dual pressure process, are described in the following sections. Table 2-1 lists all of the new and modified nitric acid plants subject to NSPS, together with their capacities and the production and NO_x abatement processes used.

2.2.1 Single Pressure Process

In the single pressure process, both the oxidation and absorption are carried out at the same pressure--either low (atmospheric) or medium pressures of 400 to 800 kPa (60 to 120 psig). Single pressure plants are the most common type in the U.S. Figure 2-1 is a simplified flow diagram of a single pressure process. A medium pressure process will be described in the following paragraphs.

Air is compressed, filtered, and preheated to about 300°C (592°F) by passing through a heat exchanger. The air is then mixed with anhydrous ammonia, previously vaporized in a continuous-steam evaporator. The resulting mixture, which contains about 10 percent ammonia by volume, is passed through the reactor. The reactor contains a platinum-rhodium (2 to 10 percent rhodium) wire-gauze catalyst (e.g., 80 mesh and 75 mm diameter wire, packed in layers of 10 to 30 sheets) so that the gas travels downward through the gauze sheets. Catalyst operating temperature is about 750°C (1382°F).

The hot nitrogen oxides and excess air mixture (about 10 percent nitrogen oxides) from the reactor are partially cooled in a heat exchanger and further cooled in a water cooler. The cooled gas is introduced into a stainless-steel absorption tower with additional air for the further oxidation of nitrous oxide to nitrogen dioxide. Small quantities of water are added to hydrate the nitrogen dioxide and also to scrub the gases. The overhead gas from the tower is reheated by feed/effluent heat exchangers and then expanded through a power recovery turbine/compressor used to supply the reaction air.* The bottom of the tower yields nitric

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*In those plants using catalytic reduction as NO_x abatement method, the tail gas is first passed through the catalytic reduction system and then expanded through a power recovery turbine/compressor used to supply the reaction air.

Table 2-1. NITRIC ACID PLANTS COMPLETED SINCE PROMULGATION OF THE NSPS

Company	Plant Location	Year Completed	Plant Design Capacity (100% HNO_3) Mg/day (tons/day)	Process Design	Emission Control System
Allied Chemical Corp.	Newell, PA	1975	164 (180)	Single Pressure	Catalytic Reduction
Monsanto Textile Co.	Escambia City, FL	1977	819 (900)	Dual Pressure	---
Nitram, Inc.	Tampa, FL	1976	310 (350)	Single Pressure	Catlytic Reduction
Kaiser Aluminum & Chem.	Savannah, GA	1976	450 (500)	Single Pressure	Extended Absorption
Columbian Nitrogen	Augusta, GA	1977	819 (900)	Single Pressure	Catalytic Reduction
Mississippi Chemical	Yazoo City, MS	1977	910 (1000)	Dual Pressure	Extended Absorption
		1973	328 (360)	Single Pressure	Extended Absorption
U.S. Army	Holston, TN	1976	285 (315)	Dual Pressure	Extended Absorption
CF Industries	Donaldsonville, LA	1977	470 (520)	Dual Pressure	Extended Absorption
IMC - Dixie Chemical	Sterlington, LA	1976	200 (220)	Single Pressure	Extended Absorption
Rubicon Chemical Inc.	Geismar, LA	1976	320 (350)	Single Pressure	Catalytic Reduction
Allied Chemical Corp.	Geismar, LA	1978	500 (550)	Single Pressure	Extended Absorption
Agrico Chemical Co.	Catoosa, OK	1975	570 (630)	Single Pressure	Chilled Absorption & Caustic Scrubbing
		1979	570 (630)		
Air Products & Chemical	Pasadena, TX	1976	289 (318)	Single Pressure	Catalytic Reduction
Dupont Co.	Victoria, TX	1977	918 (1000)	Single Pressure	Extended Absorption
Union Oil Co. of Calif.	Brea, CA	1977	137 (150)	Single Pressure	Catalytic Reduction
Valley Nitrogen	Fresno, CA	1977	180 (200)	Single Pressure	Catalytic Reduction

Table 2-1. NITRIC ACID PLANTS COMPLETED SINCE PROMULGATION OF THE NSPS (Cont'd)

Company	Plant Location	Year Completed	Plant Design Capacity (100% HNO_3) Mg/day (tons/day)	Process Design	Emission Control System
J.R. Simplot Co.	Pocatello, ID	1977	50 (53)	Single Pressure	Catalytic Reduction
Chevron Chemical Co.	Kennewick, WA	1977	500 (550)	Single Pressure	Extended Absorption
Apache Power Co.	Benson, AZ	1978	270 (300)	Dual Pressure	Extended Absorption
American Cyanamid Co.	Hannibal, MO	1978	320 (350)	Single Pressure	Extended Absorption
USS Agri-Chemicals	Crystal City, MO	1979	500 (550)	---	Extended Absorption
Gulf Oil Chemicals Co.	Jayhawk, KS	1979	910 (1,000)	Single Pressure	Extended Absorption
Chevron Chemical Co.	Fort Madison, IA	1981	500 (550)	Single Pressure	Extended Absorption
Bison Nitrogen Products	Woodward, OK	1978	250 (272)	Single Pressure	Extended Absorption
N-ReN Southwest, Inc.	Carlsbad, NM	1975	180 (195)	---	Catalytic Reduction
Badger Army Ammunition	Baraboo, WI	1981	360 (400)	Dual Pressure	Extended Absorption
N-ReN Corporation	East Dubuque, IL	1979	200 (220)	Single Pressure	Extended Absorption

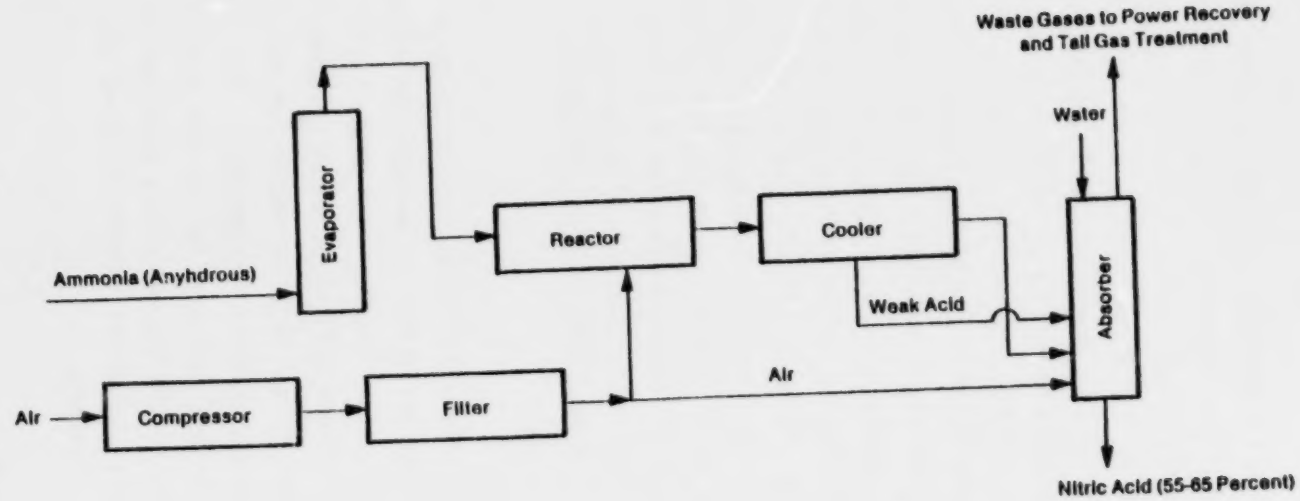


FIGURE 2-1
SINGLE PRESSURE NITRIC ACID MANUFACTURING PROCESS [1]

acid of 55 to 65 percent strength. Nineteen of the twenty-nine U.S. nitric acid plants subject to NSPS employ a single pressure process.

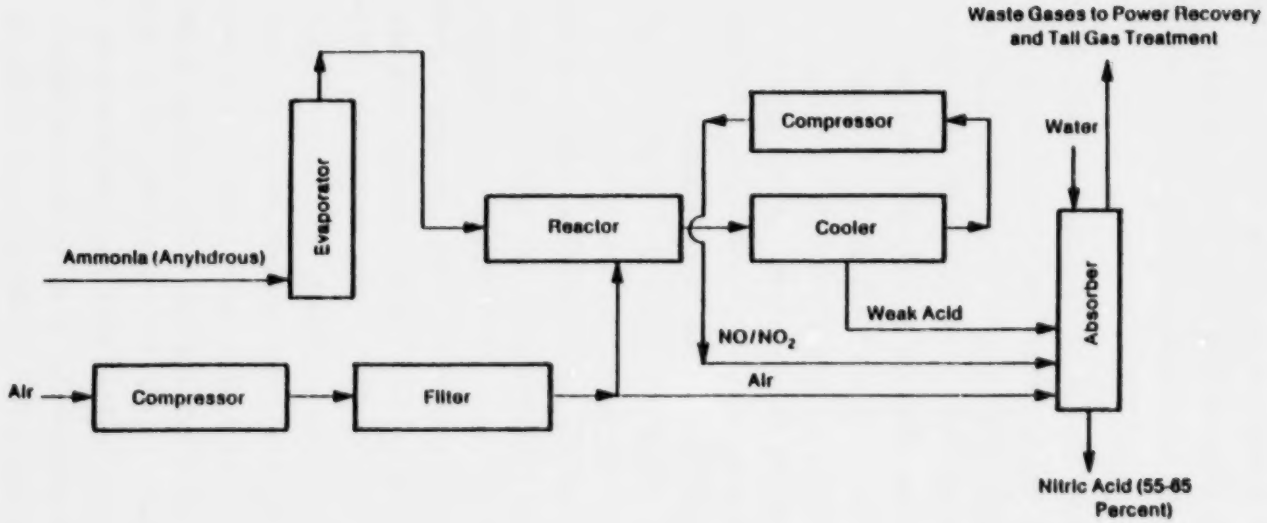
2.2.2 Dual Pressure Process

In order to obtain the benefits of increased absorption (with greater product yield) and reduced NO_x emissions, five dual pressure plants subject to NSPS have been built in the U.S.

A simplified process flow diagram for a dual pressure plant is shown in Figure 2-2. In the Uhde version of this process, liquid ammonia is vaporized by steam, heated, and filtered before being mixed with air from the air/nitrous oxide compressor at from 300 to 500 kPa (~3 to 5 atm). The ammonia/air mixture is catalytically oxidized in the reactor with heat recovery by an integral waste heat boiler to generate steam for use in the turbine-driven compressor. The combustion gases are further cooled by tail gas heat exchange and water cooling before compression to the absorber pressure of 800 to 1400 kPa (~8 to 14 atm). The absorption tower is internally water-cooled to increase absorption by water. Nitric acid up to 70 percent concentration is withdrawn from the bottom of the column and degassed with the air feed to remove unconverted NO before being sent to storage. The air/NO mixture is combined with reactor effluent to form the absorber feed. High yields of up to 96 percent conversion can be obtained by this process.

2.2.3 Strong Nitric Acid Production

The NSPS does not apply to the various processes used to produce strong acid (95-99 percent strength) by extraction or evaporation of weak acid, or by the direct strong acid process. For the most part, nitric acid is manufactured and consumed at concentrations of about 60 percent. But, concentrated (90 percent or more) nitric acid is needed for the production of chemicals such as isocyanates and nitrobenzene.[3] The rationale for excluding strong acid plants from the NSPS at the time it was developed was that, in comparison to the NO_x emissions from weak acid plants, emissions from the strong acid plants are relatively minor and only one strong acid process was in operation.[4]



Reactor Pressure: 50-75 Psi
Absorber Pressure: 120-210 Psi

FIGURE 2-2[1]
DUAL PRESSURE NITRIC ACID MANUFACTURING PROCESS

This review has found two strong acid units which have started operation since 1971.[5] Under existing State regulations,[6,7] the NO_x emissions from these strong acid plants are below the level of the NSPS. Therefore, the rationale for excluding strong acid plants is still appropriate, and this document will not further discuss strong acid plants.

2.3 EMISSIONS FROM NITRIC ACID PLANTS

The main source of atmospheric emissions from the manufacture of nitric acid is the tail gas from the absorber tower. The emissions are primarily nitric oxide and nitrogen dioxide with trace amounts of nitric acid mist. Each of these pollutants has an effect on the color and opacity of the tail gas plume. The presence of nitrogen dioxide is indicated by a reddish-brown color. Since nitric oxide is colorless, the intensity of the color and, therefore, plume opacity is directly proportional to the nitrogen dioxide concentration in the plume. A convenient rule of thumb is that a stack plume will have a visible brown color when the NO_2 concentration exceeds 6,100 ppm divided by the stack diameter in centimeters.[2] This means that the threshold of visibility for a 5-cm diameter stack is about 1200 ppm of NO_2 and for a 30-cm stack, 200 ppm of NO_2.

The opacity of the plume is also a function of the amount of nitric acid mist in the tail gas, which is dependant on the type of process used, the extent of mist entrainment, and the efficiency of entrainment separators. For those acid processes operated above atmospheric pressure, the tail gases are reheated and expanded for power recovery purposes and discharged to the atmosphere at 200° to 250°C (392° to 482°F). At this temperature, any acid mist present is converted to the vapor state. In atmospheric pressure processes, however, the temperature of the tail gas is below the dew point of nitric acid. As a result, the acid is emitted as a fine mist which increases the plume opacity. The average emission factor for uncontrolled acid plants is 20 to 28 kg NO_x/Mg (40 to 56 lb NO_x/ton) of acid, with typical uncontrolled tail gas concentrations on the order of 3000 ppm NO_x. This concentration would be experienced in a low pressure plant. The NO_x concentration in the tail gas of medium pressure plants ranges from 1000 to 2000 ppm.

Nitrogen oxide emissions vary considerably with changes in plant operation. Several operating variables have a more significant effect on increasing NO_x emissions. These include: (1) insufficient air supply to the oxidizer and absorber; (2) low pressure, especially in the absorber; (3) high temperatures in the cooler-condenser and absorber; (4) production of an excessively high-strength product acid; and (5) operation at high throughput rates. Finally, faulty equipment, such as compressors or pumps, lead to lower pressures and leaks which decrease plant efficiency and increase emissions.

2.4 INDUSTRY CHARACTERIZATION

2.4.1 Geographic Distribution

In 1972 there were approximately 125 nitric acid units in existence, exclusive of government-owned units at ordnance plants. About 75 percent of these units were 10 years old or older and, in general, had capacities of 270 Mg/day (300 tons/day) or less. The remaining 25 percent of the units were of more recent and larger design, having capacities exceeding 270 Mg/day (300 tons/day). The Bureau of the Census reported that there were 72 plants (involving one or more units) in 1972 producing nitric acid in the U.S. and that by 1977 the net number of plants in production had increased by only one.

The largest consumer of nitric acid is the fertilizer industry which consumes 70 percent of all nitric acid produced; industrial explosives use 15 percent of acid produced. Other end uses of nitric acid are gold and silver separation, military munitions, steel and brass pickling, photoengraving, production of nitrates, and the acidulation of phosphate rock.

As of March 1983, 29 nitric acid units subject to NSPS had come on-stream. The heaviest concentration of new or modified nitric acid unit construction since 1971 appears along the coast of the Gulf of Mexico and within the Mississippi River delta. The distribution of nitric acid plants displays a spacial pattern similar to that of the major fertilizer production centers. Since the bulk of all nitric acid produced is consumed

captively in the manufacture of nitrogen fertilizer used mainly in the Midwest cornbelt, the South Central States, and the Southwest, the similarity in spacial patterns between nitric acid plants and fertilizer manufacturing plants is to be expected.

2.4.2 Production

In 1971, U.S. production of 100 percent nitric acid totalled 6,928,000 megagrams (7,638,000 tons)[8] and increased to 8,200,000 megagrams (9,040,000 tons) in 1981.[9]

The average rate of production increase for nitric acid fell from 9 percent/year in the 1960-1970 period to 1.7 percent from 1971 to 1981. The decline in demand for nitric acid parallels that for nitrogen-based fertilizers during the same period.

In 1971, the EPA predicted the start-up of five new nitric acid units per year for several years after promulgation of the NSPS. The actual average rate of start-up between 1971 and 1982 has been between two and three units per year.

2.4.3 Trends

About 50 percent of plant capacity in 1972 consisted of small to moderately sized units (50 to 300 ton/day capacity). Because of the economics of scale, some producers are electing to replace their existing units with new, larger units. Also, the trend toward reduction of NO_x emissions is stimulating the shutdown and replacement of older units. New nitric acid production units have been built as large as 910 Mg/day (1000 tons/day). The average size of new units is approximately 430 Mg/day (500 tons/day).

2.5 SELECTION OF NITRIC ACID PLANTS FOR NSPS CONTROL

Nitric acid plants were originally selected for NSPS development because they can be large point sources of nitrogen oxides (NO_x). Without emission control, a modern plant producing 454 megagrams (500 tons) per day of nitric acid would release about 454 kilograms (1,000 pounds) of NO_x per hour at a concentration of 3,000 ppm by volume. The growth rate was projected to be five new units per year. As stated above, the actual growth rate has been about three units per year.

2.6 REFERENCES

1. A Review of Standards of Performance for New Stationary Sources - Nitric Acid Plants, U.S. Environmental Protection Agency, EPA-450/3-79-013, March 1979.

2. Control Techniques for Nitrogen Oxides Emissions from Stationary Sources - Revised Second Edition, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, EPA-450/3-83-002, January 1983.

3. Concentrating Nitric Acid By Surpassing An Azeotrope, L. M. Marzo and J. M. Marzo, Chemical Engineering, November 3, 1980, pp. 54-55.

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6. Telephone conversation between B. Sigmore, West Virginia Air Pollution Control Commission, and J. Eddinger, U.S. EPA, on July 1, 1983.

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3.0 CURRENT STANDARDS FOR NITRIC ACID PLANTS

3.1 FACILITIES AFFECTED

The NSPS regulates nitric acid plants that were planned or under construction or modification as of August 17, 1971. Each nitric acid production unit (or "train") is the affected facility. The standards of performance apply to new facilities producing so-called "weak nitric acid" (defined as 50 to 70 percent strength). The standards do not apply to the various processes used to produce strong acid by extraction or evaporation of weak acid, or by the direct strong acid process.

An existing nitric acid plant is subject to the NSPS if: (1) it is modified by a physical or operational change in an existing facility thereby causing an increase in the emission rate to the atmosphere of any pollutant to which the standard applies, or (2) if in the course of reconstruction of the facility, the fixed capital cost of the new components exceeds 50 percent of the cost that would be required to construct a comparable entirely new facility that meets the NSPS.

3.2 CONTROLLED POLLUTANTS AND EMISSION LEVELS

Total nitrogen oxide emissions from nitric acid plants are controlled under the NSPS, as defined by 40 CFR 60, Subpart G (as originally promulgated in 36 FR 24881 with subsequent modifications in 39 FR 20794):

> (a) On and after the date on which the performance test required to be conducted . . . is completed, no owner or operator subject to the provisions of this subpart shall cause to be discharged in to the atmosphere from any affected facility any gases which:
>
> (1) Contain nitrogen oxides, expressed as NO_2, in excess of 1.5 kg per metric ton of acid produced; (3.0 lb per ton), the production being expressed as 100 percent nitric acid.
>
> (2) Exhibit 10 percent opacity, or greater.

3.3 TESTING AND MONITORING REQUIREMENTS

3.3.1 Testing Requirements

Performance tests to verify compliance with the NO_x standard must be conducted within 60 days after the plant has reached its full capacity production rate, but not later than 180 days after the initial start-up of the facility (40 CFR 60.8). The EPA reference methods (40 CFR 60, Appendix A) to be used in conjunction with NO_x compliance testing include:

1. Method 7 for the concentration of NO_x
2. Method 1 for sample and velocity transverses
3. Method 2 for velocity and volumetric flow rate
4. Method 3 for gas analysis

Each performance test consists of three runs, each consisting of at least four grab samples taken at approximately 15-minute intervals. The arithmetic mean of the runs constitutes the value used to determine whether the plant is in compliance.

Method 7A (Ion Chromatograph) has been proposed as an alternative method for Method 7 for determining compliance with the NSPS. Method 7A offers improvements over Method 7 in that the sample analytical time is shortened and precision is improved. This method utilizes the evacuated flask sampling procedure outlined in Method 7, and the recovered sample is then analyzed by ion chromatograph.

Acid produced, expressed in tons per hour of 100 percent nitric acid is required to be determined during each testing period by suitable methods and shall be confirmed by a material balance over the production system. The method generally used to determine acid production by the plants reviewed during this study is flowmeters. Other methods used are acid inventory, calculations based on air flow or ammonia flow, and weighting the acid produced over a certain interval.

3.3.2 Monitoring Requirements

The NO_x levels in the tail gas from new nitric acid plants are required to be continuously monitored to provide: (1) a record of performance and (2) information to plant operating personnel such that suitable corrections can be made when the system is out of adjustment. Plant operators are

required to maintain the monitoring equipment in calibration and to furnish records of excess NO_x emission values to the Administrator of the EPA or to the responsible State agency as requested.

The continuous monitoring system is calibrated using a known air NO_2 gas mixture as a calibration standard. Performance evaluation of the monitoring system is conducted using the EPA Method 7. In general, the system in use should satisfy the specifications as shown in 40 CFR 60, Appendix B, Performance Specification 2.

The operator is required to establish a conversion factor for the purpose of converting the monitoring data into units of the standard. The conversion factor is to be established by measuring emissions with the continuous monitoring system concurrent with measuring emissions with the reference method tests.

The production rate and hours of operation are also required to be recorded daily.

Excess NO_x emissions are required to be reported to the EPA (or appropriate State regulatory agencies) for all 3-hour periods of excess emissions (or the arithmetic average of three consecutive 1-hour periods). Periods of excess emission are considered to occur when the integrated (or arithmetic average) plant stack NO_x emission exceeds the 1.5 kg/Mg (3 lb/ton) standard.

4. STATUS OF CONTROL TECHNOLOGY

The methods of emission control being employed on nitric acid units subject to the NSPS are presented in this chapter. As discussed in Chapter 2, the NO_x content of the tail gas in any nitric acid plant is a function of the extent to which the absorption reaction reaches completion. Nitric acid plants can be designed for low NO_x emission levels without any add-on processes. Such plants are usually designed for high absorber efficiency; high inlet gas pressures and effective absorber cooling. However, some new plants are not designed for NO_x emission levels low enough to meet the NSPS. For these plants, add-on abatement methods are necessary. Therefore, to achieve the NSPS, nitric acid plants must extend the absorption reaction, add a control device to the exhaust stream, or both.

The control methods used by units subject to the NSPS include extended absorption, catalytic reduction, and chilled absorption with caustic scrubbing. Catalytic reduction was used as the basis for the NSPS. Since that time fuel costs have risen, and all but one of the units which have started operation since the 1979 review are designed for high absorber efficiency (extended absorption).

4.1 EXTENDED ABSORPTION

The most obvious method of reducing NO_x emissions in the tail gas of a nitric acid plant is to increase the absorption efficiency. Emission control by absorption is somewhat misleading, since no add-on emission control equipment is necessary if the plant is designed and built with sufficient absorption capacity. Nitric acid plants have been constructed with absorption systems designed for 99.7 plus percent NO_x recovery.

In the extended absorption process, the increased absorption capacity is achieved by installing a single larger absorber or adding a second absorption tower in series to the existing absorber. The NO_x is

absorbed by water and forms nitric acid. The economics of the extended absorption process generally require the inlet gas pressure at the absorber to be at least 730 kPa (107 psig).[1] There is normally no liquid effluent from extended absorption; the weak acid from the secondary absorber is recycled to the first absorber, increasing the yield of nitric acid. Figure 4-1 is a schematic flow diagram of a nitric acid plant using extended absorption by means of a second absorber. Figure 4-2 is a schematic flow diagram of a unit using only a single larger absorber for emission control.

A smaller volume and number of trays in the absorption system are required when the use of mechanical refrigeration for chilling part of the cooling water is employed. Two cooling water systems are used for cooling the absorbers. The first part of the absorption process is cooled by the normal cooling water available at the plant site. Approximately one-third of the trays are cooled by normal cooling water. The balance of the trays in the absorption system are cooled by cooling water at about 7°C (45°F), which is achieved by mechanical refrigeration. The refrigeration process is normally a part of the ammonia vaporization section of the nitric acid plant.

The extended absorption system operates without any problems as long as design conditions are met. This means that the absorber pressure and oxygen content in the gas to the absorber must not be below design level, and the temperature and NO_x content in the gas stream must not exceed design level. With regard to temperatures, this system is vulnerable to high summer ambient temperatures in the southern tier of States, i.e., temperatures in excess of 35°C (95°F). Information from several extended absorption nitric acid plants confirms this potential problem. The plants indicated, however, that they have compensated for these periods of excessive ambient temperatures by designing the unit to allow them to decrease cooling water temperature or by increasing the bleach and secondary air flow.[2,3,4]

Of the 10 nitric acid plants that have started operation since the 1979 review, 8 feature extended absorption as the NO_x control mechanism. It appears that the increases in natural gas prices have made extended

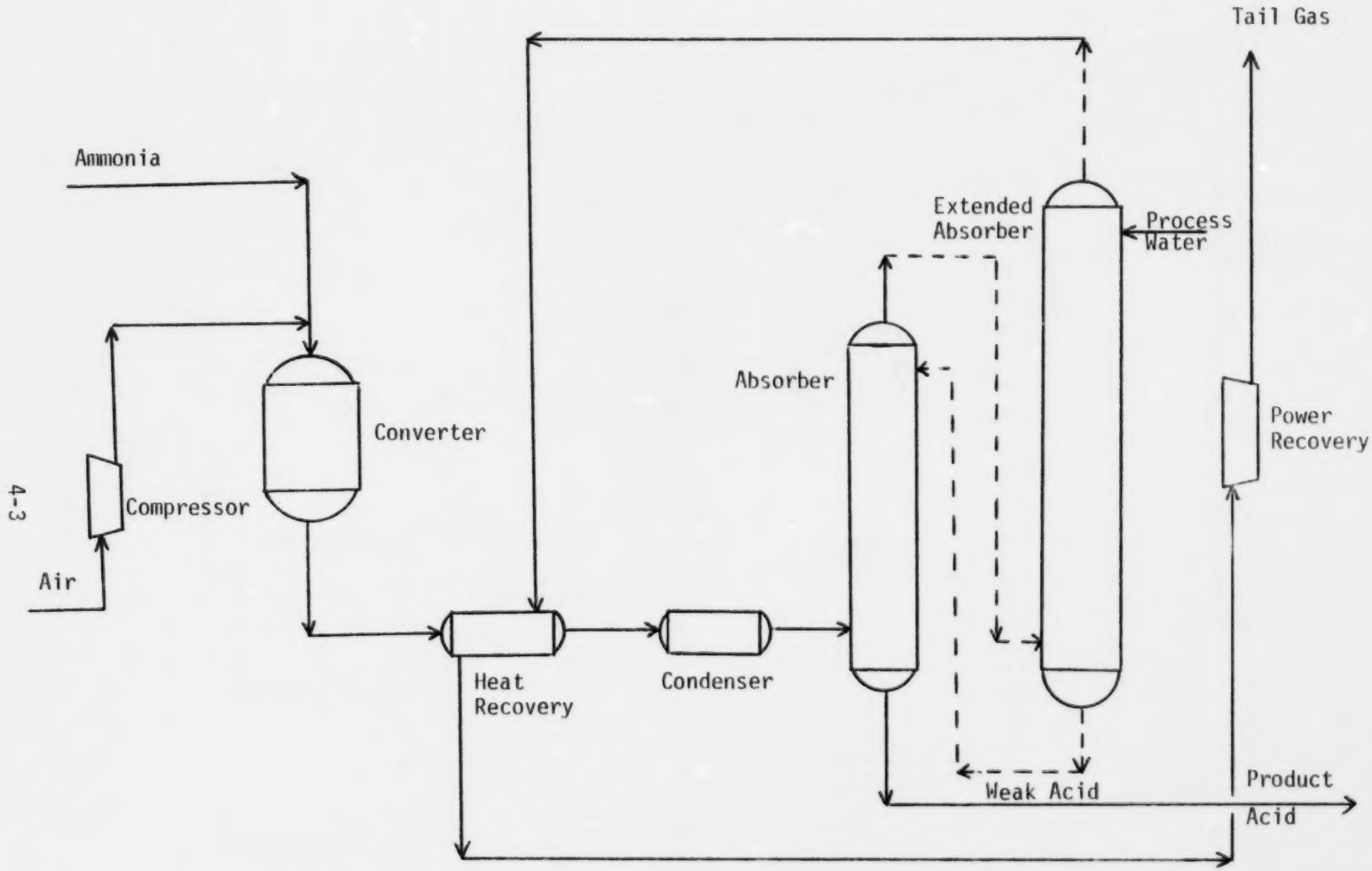

Figure 4-1. EXTENDED ABSORPTION SYSTEM USING SECOND ABSORBER FOR NO_x CONTROL

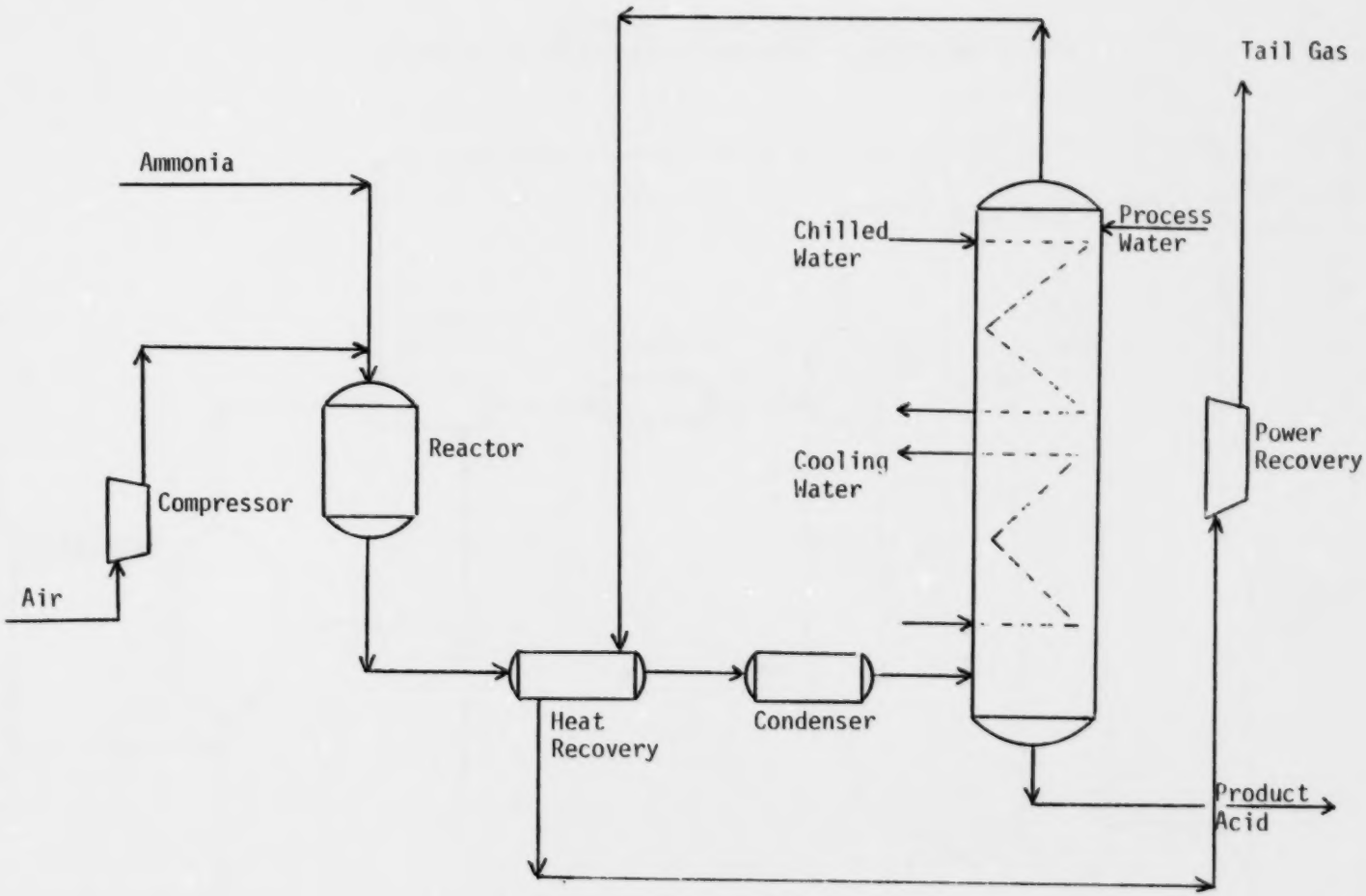

Figure 4-2. EXTENDED ABSORPTION SYSTEM USING ONE LARGE ABSORBER FOR NO_x CONTROL

absorption the preferred process for NO_x abatement in the future. In fact, one plant using catalytic reduction indicated that if they were to install a new acid plant, they would probably use the extended absorption because of the lower operating costs.[5]

4.2 CATALYTIC REDUCTION

Catalytic reduction was widely used as an NO_x abatement system on new nitric acid plants built between 1971 and 1977. Due to rapid fuel price escalations since 1975, new installations have chosen extended absorption. Catalytic reduction was also used as a method of NO_x decolorization on over 50 percent of the nitric acid plants built prior to the NSPS. The reasons for the prevalence of this control technology until 1975 were:

(1) Its relative ease and flexibility of operation.

(2) The recovery of waste heat.

(3) High NO_x removal efficiencies.

(4) Relatively cheap cost of fuel.

In practice, the catalytic reduction unit is an integral part of the plant (Figure 4-3). The tail gas from the absorption tower is preheated by heat exchange with the converter effluent gas. Fuel is added and burned in the catalytic unit to generate heat and reduce the NO_x concentration in the tail gas. The hot gas from this unit passes to an expander which drives the process air compressor for the ammonia converter. A waste heat boiler removes the heat from the expander outlet gas in the form of steam, and the treated tail gas is vented to the atmosphere. In some cases, a waste heat boiler is required after the catalytic unit to keep the expander inlet temperature below its design maximum--usually 677°C (1,250°F).

Catalytic reduction processes can be divided into two categories: nonselective and selective reduction. In nonselective reduction, the tail gas from the absorber is heated to the necessary ignition temperature and mixed with a fuel such as methane, carbon monoxide, or hydrogen. When methane (natural gas) is used as the fuel, the following reactions take place:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (1)$$

$$CH_4 + 4NO_2 \rightarrow 4NO + CO_2 + 2H_2O \qquad (2)$$

$$CH_4 + 4NO \rightarrow 2N_2 + CO_2 + 2H_2O \qquad (3)$$

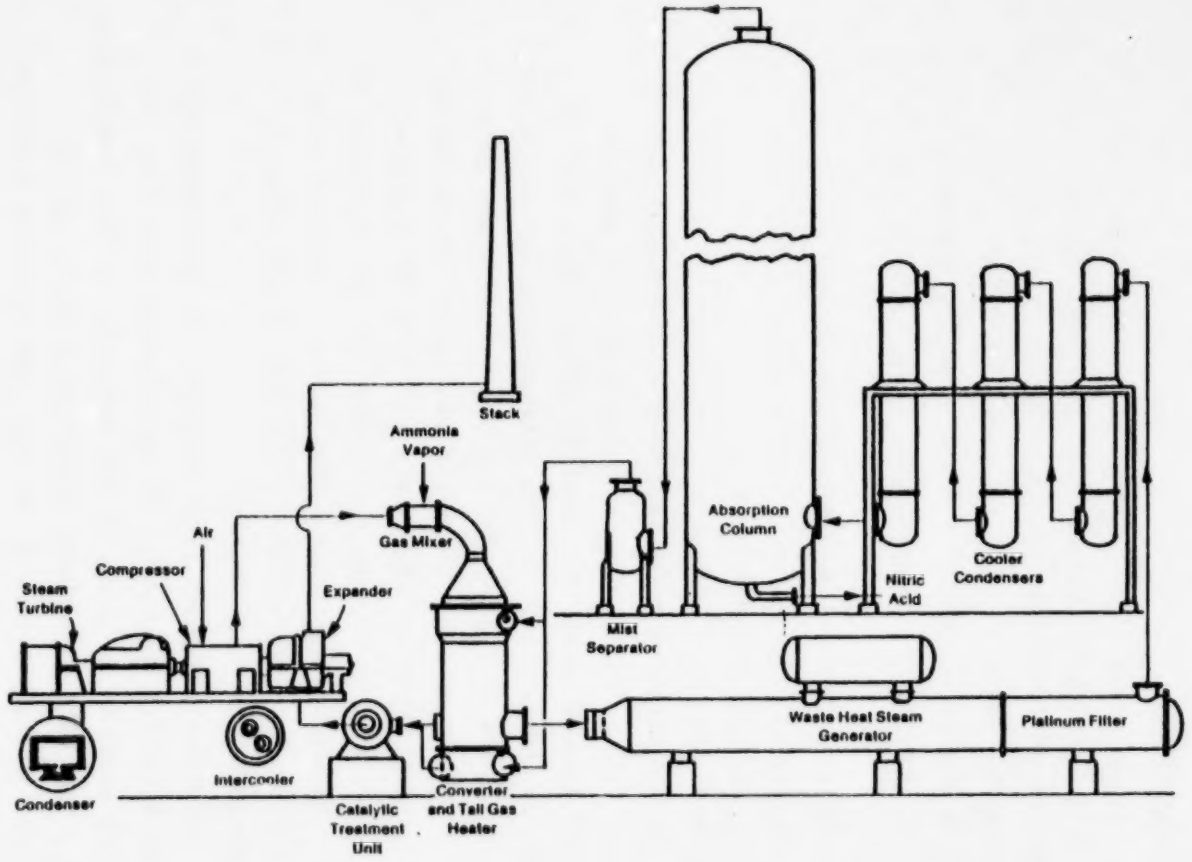

FIGURE 4-3.
ACID PLANT INCORPORATING CATALYTIC REDUCTION FOR NO_x ABATEMENT [1]

The first two reactions proceed rapidly with the evolution of heat which is recovered in a waste heat boiler. In the second reaction, or decolorization step, the nitrogen dioxide is converted to nitric oxide, so the gas is colorless even though there has been no decrease in the total nitrogen oxides. Only the last reaction with additional methane results in the reduction of the nitric oxide to nitrogen. The final reduction step must be limited to an upper temperature of 843°C (1,550°F), due to the catalyst thermal limitation. If reduction has to be carried out in the presence of high oxygen concentrations (above 3.0 percent), it must be performed in two stages to prevent exceeding the upper temperature limit. In practice, 98 percent control efficiency of the NO_x in the tail gas has been achieved by this process.[5]

In the selective reduction process, ammonia is used to catalytically reduce NO_2 to N_2 without simultaneously reacting with oxygen. A ceramic-supported platinum catalyst is used to effect the following reactions:

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$$

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O$$

Both of these reactions occur at relatively low temperatures (210° to 270°C).

The advantage of this method is that less heat is evolved and the installation of heat removal equipment is unnecessary. However, the catalyst required is more expensive and the ammonia cost may not be competitive with other fuels even when less is required. Close temperature control is required to prevent ammonia oxidation, which would increase nitrogen oxide emissions. Startup and shutdown procedures must also be closely controlled to avoid formation of ammonium nitrate salts.

Of the 10 nitric acid plants subject to the NSPS which have started operation since the 1979 review, only 1 features catalytic reduction as the NO_x control method. This plant uses natural gas as the fuel.

4.3 CAUSTIC SCRUBBING

Caustic scrubbing involves treatment of the absorber tail gas with solutions of sodium hydroxide to absorb NO and NO_2 in the form of nitrate and/or nitrite salts in a scrubbing tower. In caustic scrubbing, the following reactions take place:

$$2NaOH + 3NO_2 \rightarrow 2NaNO_3 + NO + H_2O$$

$$2NaOH + NO + NO_2 \rightarrow 2NaNO_2 + H_2O$$

However, disposal of the spent scrubbing solution presents a serious water pollution problem. One nitric acid plant subject to the NSPS employs a combination of chilled extended absorption and caustic scrubbing to achieve NO_x abatement. At this unit, the caustic scrubber (Figure 4-4) is located in the top of the absorber. The caustic solution is recycled in the scrubber with a portion bled to the absorber. This caustic bleed-off results in an acid loss.[6]

4.4 REFERENCES

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2. Letter and enclosure from F. W. Berryman, Chevron Chemical Company, to Jack R. Farmer, U.S. EPA, dated March 16, 1983.

3. Letter and enclosure from Joseph M. Homan, Terra Chemicals International, Inc., to Jack R. Farmer, U.S. EPA, dated March 1, 1983.

4. Letter and enclosure from Ben T. Traywick, Apache Powder Company, to Jack R. Farmer, U.S. EPA, dated February 24, 1983.

5. Trip Report - Columbia Nitrogen Corporation, Augusta, Georgia, February 16, 1983.

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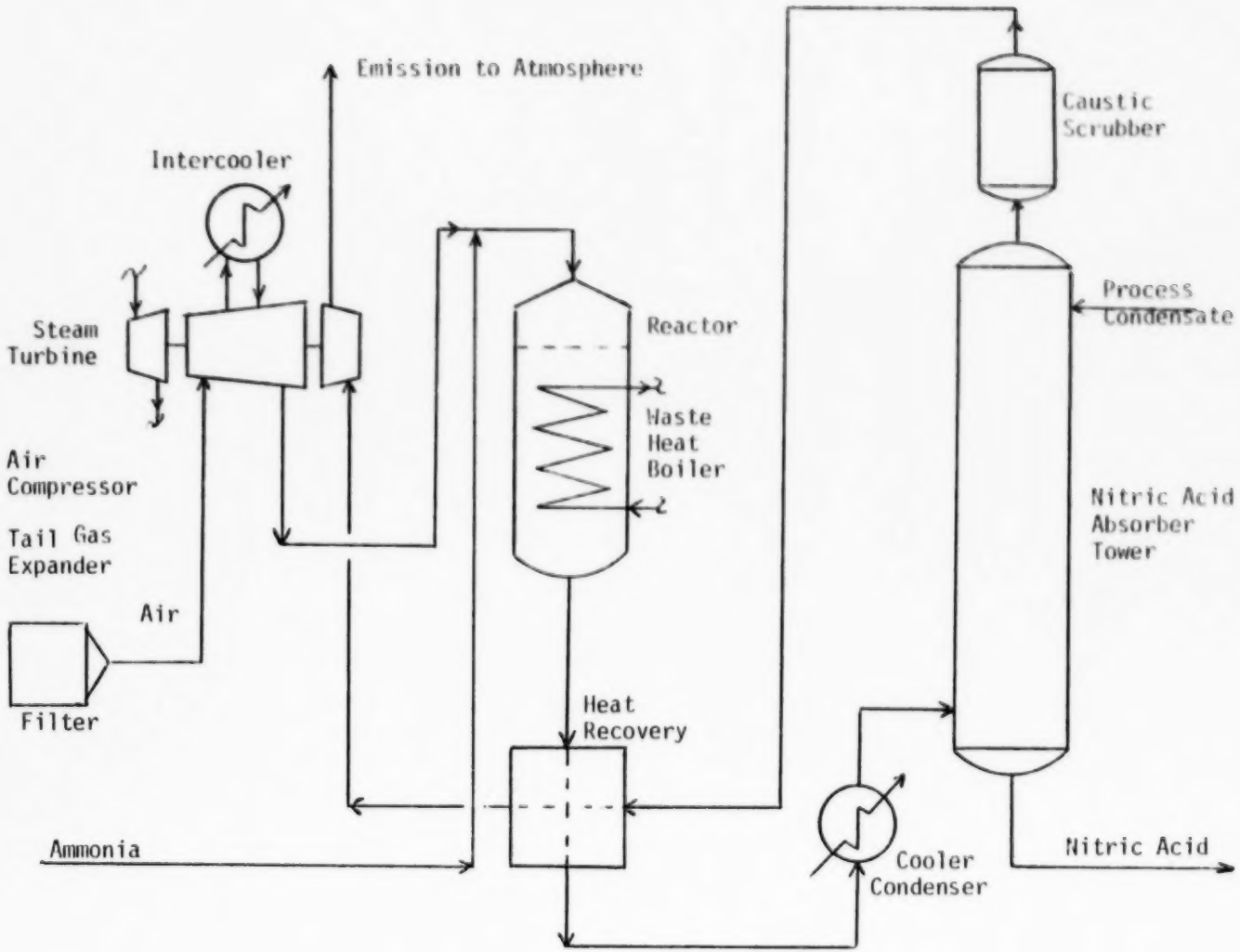

Figure 4-4. SCHEMATIC OF NITRIC ACID PLANT INCORPORATING CAUSTIC SCRUBBING FOR NO_x CONTROL[6]

5. COMPLIANCE TEST RESULTS

EPA regional offices, State agencies, and nitric acid plants were contacted to obtain compliance test information for facilities which are subject to the NSPS and have started operation since the 1979 review.

The results of the survey show that there are 10 new nitric acid units which have started operation since the 1979 review. Data obtained include the average NO_x emissions and the 100 percent nitric acid production rates at the time of the tests. Also obtained were quarterly emission monitoring reports for 1981 and 1982.

5.1 ANALYSIS OF NSPS COMPLIANCE TEST RESULTS

The results of compliance tests obtained from new nitric acid plants are summarized in Table 5-1. Compliance test results from the 10 nitric acid units indicate that all but one unit are in compliance with the NSPS. The units are controlled by either catalytic reduction, extended absorption, or chilled absorption and caustic scrubbing.

The nitric acid unit which is not yet in compliance with the NSPS is utilizing extended absorption and has never completed the start-up phase. This unit is owned by the U.S. Army and is installed for ammunition production. The unit has never been operated except for a two-day start-up period during which time the unit was compliance tested and shut down. Discussions with plant personnel indicate that there are no plans to restart the unit.[1] It is installed as a standby unit for ammunition production during wartime. The plant personnel also indicated that modifications would be made to bring the unit into compliance prior to any startup. However, due to budget limitations, these modifications cannot be scheduled until 1987.

Table 5-1. COMPLIANCE TEST RESULTS FOR NITRIC ACID PLANTS SUBJECT TO THE NSPS SINCE THE 1979 REVIEW[2-11]

Plant	Control Technique	Average NO_x Emissions (lb/ton)
A	Chilled Absorption & Caustic Scrubbing	1.84
B	Catalytic Reduction	1.13
C	Extended Absorption	1.3
D	Extended Absorption	2.75
E	Extended Absorption	1.8
*F	Extended Absorption	4.1
G	Extended Absorption	2.55
H	Extended Absorption	2.81
I	Extended Absorption	2.74
J	Extended Absorption	2.13

NSPS = 3.0

* Plant tested upon start-up, was then shutdown, and has not restarted.

5.2 ANALYSIS OF NO_x MONITORING RESULTS

Quarterly emission monitoring reports for 1981 and 1982 were obtained on seven nitric acid plants subject to the NSPS which have come on-line since the 1979 review. Table 5-2 summarizes these quarterly reports. Five of the seven units have maintained emissions below the NSPS 95 percent of the time or greater during the two-year period. The excess emissions generally occurred during startups and shutdowns due to forced plant outages. Other causes of excess emissions were problems with the chilling system, high cooling water temperature, and leaks in the tail gas heater. Leaks in the heater allow NO_x-rich gas to leak into the exhaust gas downstream of the pollution control equipment. Leaks in the expander gas heater were the principal cause of the excess emissions for the other two units (Plants E and H). Plant E maintained emissions below the NSPS only 90 and 80 percent of the time in 1981 and 1982, respectively. The reheater leak at Plant E occurred in the last quarter of 1981 and was not corrected until the second quarter of 1982. This unit maintained emissions below the NSPS over 97 percent of the time in the first three quarters of 1981, and returned to a high reliability of maintaining emissions below the NSPS in the last two quarters of 1982.

Plant H has experienced problems in continuously operating with emissions below the NSPS since startup of the unit in 1979. The initial compliance test conducted in August 1980 indicated an emission rate of 3.17 pounds per ton. This unit generally maintained emissions below the NSPS until a leak developed in the expander gas heater in late 1980. Monitoring data prior to the leak indicated to the company that they could not maintain 60 percent acid strength (design level) and maintain emissions below the NSPS. Therefore, the acid strength was reduced. The leak in the expander gas heater was repaired at the end of the first quarter of 1981. The unit was then again operating with emissions below the NSPS. A second compliance test conducted in April 1981 indicated an NO_x emission rate of 2.81 pounds per ton. The unit operated with emissions below the NSPS, for the most part, in the second quarter of 1981. With the arrival of hot weather in June, the company was unable to keep the emissions below the NSPS on a continuous basis. In August 1981,

Table 5-2. SUMMARY OF NO_x MONITORING DATA FOR NITRIC ACID PLANT SUBJECT TO THE NSPS[2-8]

Plant	Percent of Time in Compliance 1981	1982	Total Hours In Excess of NSPS	Hours in Excess due to Startup or Shutdown	Principal Cause of Excess Emissions
A	99.8	99.7	39	24	Forced plant outages
C	98.0	98.9	230	159	Forced plant outages
D	99.6	97.2	97	63	
E	90.2	79.8	2,380	44	Leak in Reheater
G	96.3	95.8	328	164	1) High cooling water temperature 2) Leak in tail gas heater
H	43.4	1.0	6,281	681	Leak in expander gas heater
I	95.9	96.1	389	117	Chiller problems

several modifications were made to the unit in an effort to increase the absorption tower efficiency and, thus, decrease NO_x emissions. These modifications included reducing the acid concentration to 54 percent, adding potassium carbonate to the chilled water system to lower the water temperature without freezing up the system, increasing the pressure on the absorption system by closing back on the hot gas expander inlet valve, and by operating the compressor set at the fastest speed possible at all times to maintain the highest air pressure possible. These modifications resulted in the unit achieving the NSPS during the winter months (low ambient temperatures) until leaks developed again in the expander gas heater. The leaks are felt to be caused by the thermal stressing in the unit due to the extreme temperature differences between unit operation and unit shutdown. The plant made several attempts to repair the leaks; and it was determined that the main expander support springs on the expander gas heater failed, and that this lack of support for the unit had created stresses and possible misalignment in the tube sheet resulting in the tube sheet cracking. These leaks caused excess emissions from the fourth quarter of 1981 until the plant was shutdown in the second quarter of 1982. In mid-August 1982, the unit was brought back on-line. The corrective action taken in the expander gas heater reportedly eliminated the problems encountered with the leaks. However, additional process design modifications failed to bring the NO_x emissions down to the level of the NSPS. Due to the current economic situation, the unit was shutdown indefinitely in September 1982.

Discussion with a vendor representative confirmed that the high NO_x emissions at Plant H were caused by leaks, but that a further problem exists because the design pressure [850 kPa (125 psig)] is not being achieved.[12] The vendor stated that the design of this unit is similar to other units in operation, and it is designed for operation during the summer high ambient temperatures. The vendor was prepared to perform tests during the hot months to determine the results of the latest modifications, but these were cancelled when the unit was shutdown and not

restarted due to economic conditions. The vendor indicated that there are no plans for further modifications until the unit is started up and results of the latest modifications have been analyzed.

Monitoring reports for 1981 and 1982 were obtained on one nitric acid plant subject to the NSPS which is controlled by catalytic reduction. The data showed that the unit maintained emissions below the NSPS over 99.7 percent of the time in both 1981 and 1982.

5.3 STATUS OF NO_x EMISSION MONITORS

The NSPS requires installation of an instrument for continuously monitoring and recording NO_x emissions. The continuous monitor in wide use is based on the principle of photometric analysis. The monitors installed on nitric acid plants subject to the NSPS have been very reliable according to those plants that have started operation since the 1979 review. Three plants have reported greater than 98 percent reliability.[4,5,8] Routine maintenance on the monitor is reported to be about one manhour per week.[3,8] The main problem has been deterioration of the ultraviolet lamp resulting in frequent replacement. These monitors have been installed for emissions monitoring only.

The continuous monitoring system is calibrated using a known air-NO_2 gas mixture as a calibration standard. Performance certification of the monitoring system is conducted using the EPA Method 7. In general, the system in use should satisfy the specifications as shown in 40 CFR 60, Appendix 3, Performance Specification 2.

5.4 REFERENCES

1. Telephone Conversation between Don Hartman, Badger Army Ammunition Plant, and James Eddinger, U.S. EPA, on January 17, 1983.

2. Letter and enclosure from J. Brad Willett, American Cyanamid Company, to Jack R. Farmer, U.S. EPA, dated April 29, 1983.

3. Letter and enclosure from F. W. Berrymen, Chevron Chemical Company, to Jack R. Farmer, U.S. EPA, dated March 16, 1983.

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5. Letter and enclosure from Ben T. Traywick, Apache Powder Company, to Jack R. Farmer, U.S. EPA, dated February 24, 1983.

6. Trip Report - Gulf Oil Chemicals Company, Jayhawk, Kansas, February 8, 1983.

7. Letter and enclosure from Kenneth E. Jury, N-ReN Corporation, to Jack R. Farmer, U.S. EPA, dated March 4, 1983.

8. Letter and enclosure from Joseph M. Homan, Terra Chemical International, Inc., to Jack R. Farmer, U.S. EPA, dated March 1, 1983.

9. Letter and enclosure from Jack S. Divita, U.S. EPA-Region VI, to Stanley T. Cuffe, U.S. EPA, dated November 24, 1982.

10. Memo from J. Brian Galley, Wisconsin Department of Natural Resources, to Jim Eddinger, U.S. EPA, dated November 8, 1982.

11. Trip Report - U.S. EPA-Region VII Office, Kansas City, Missouri, February 9, 1983.

12. Telephone Conversation between Glenn Smith, D.M. Weatherly Company and James Eddinger, U.S. EPA, on March 3, 1983.

6. COST ANALYSIS

This chapter presents the updated costs of control systems required to achieve the current NSPS covering nitric acid plant tail-gas emissions. Two control systems are analyzed: (1) the extended absorption process and (2) the catalytic reduction process. Capital and annualized costs of each control option are estimated for three model plant sizes: 181, 454, and 907 megagrams (200, 500, and 1000 tons) of nitric acid production (100 percent basis) per day. The cost data are presented in January 1983 dollars, and the developed costs are compared with actual costs reported by the industry.

The control system includes all the equipment and auxiliaries required to provide the specified emission control. The capital cost of a control system includes all the cost items necessary to design, purchase, install, and commission the control system. In addition to the direct costs, the capital cost includes such indirect items as engineering, contractor's fee, construction expense, and a contingency.

The annualized cost represents the cost of owning and operating the control system. The operating cost covers the utilities, supplies, and labor required to operate and maintain the system on a day-to-day basis. The cost of owning the system includes capital-related charges such as capital recovery, property taxes, insurance, and administrative charges.

6.1 EXTENDED ABSORPTION PROCESS

6.1.1 Capital Costs

The costs of an extended absorption process are estimated for the three model plant sizes. The costs represent the incremental costs of achieving the New Source Performance Standard compared with an uncontrolled plant. The control system consists of a secondary absorber and condensation system for recovery of absorbed nitric acid. The most important of several design alternatives to be considered are the tail-gas pressure and temperature and the temperature of the gas leaving the secondary absorber. Some plants use only well water in the absorption tower,

whereas others use refrigerated or chilled water. The tail-gas pressure determines the shell thickness of the absorber, and the temperatures generally affect the gas flow rate and hence the absorber size. Figure 6-1 shows the basic conditions for the theoretical system used in this study. All gas and liquid volumes and the absorber volume are proportional to plant capacity. Regardless of its size, the absorber, a bubble-tray column, has 39 trays. Figure 6-2 presents a schematic of the entire extended absorption system. The condensation system includes a chiller, compressor, condenser, chilled water tank, and necessary pumps and piping. Estimates of the capital costs of the absorption system are based on published cost data.[1,2] The purchase cost of each system component was estimated, and installation, labor, and material were added to obtain the total installed cost. This cost includes all the necessary ancillaries, such as foundations, insulation, and ladders. The indirect costs were factored from the direct costs. All of these costs and factors were taken from References 1 and 2 and updated to January 1983 dollars per the Chemical Engineering (CE) Plant Cost Index. Tables 6-1 through 6-3 show capital costs of an extended absorption system for the three model plants. These cost estimates define the curve shown in Figure 6-3. This figure also shows the capital costs reported by four plants (updated to January 1983 dollars) in their responses to EPA information requests. This figure indicates a close correlation between estimated and reported costs.

6.1.2 Annualized Costs

The annualized costs include the direct operating costs for the pumps, water chiller, and absorber. Utilities and direct operating labor costs are based on the following estimates:

Cost element	Plant size, Mg/day		
	181	454	907
Water, m^3/s	0.0032	0.0090	0.016
Electricity, GJ/yr	4300	10900	23400
Labor, h/yr	2150	3225	4300
Pumps, GJ/yr	1200	3100	7900
Chiller, GJ/yr	3100	7800	15500

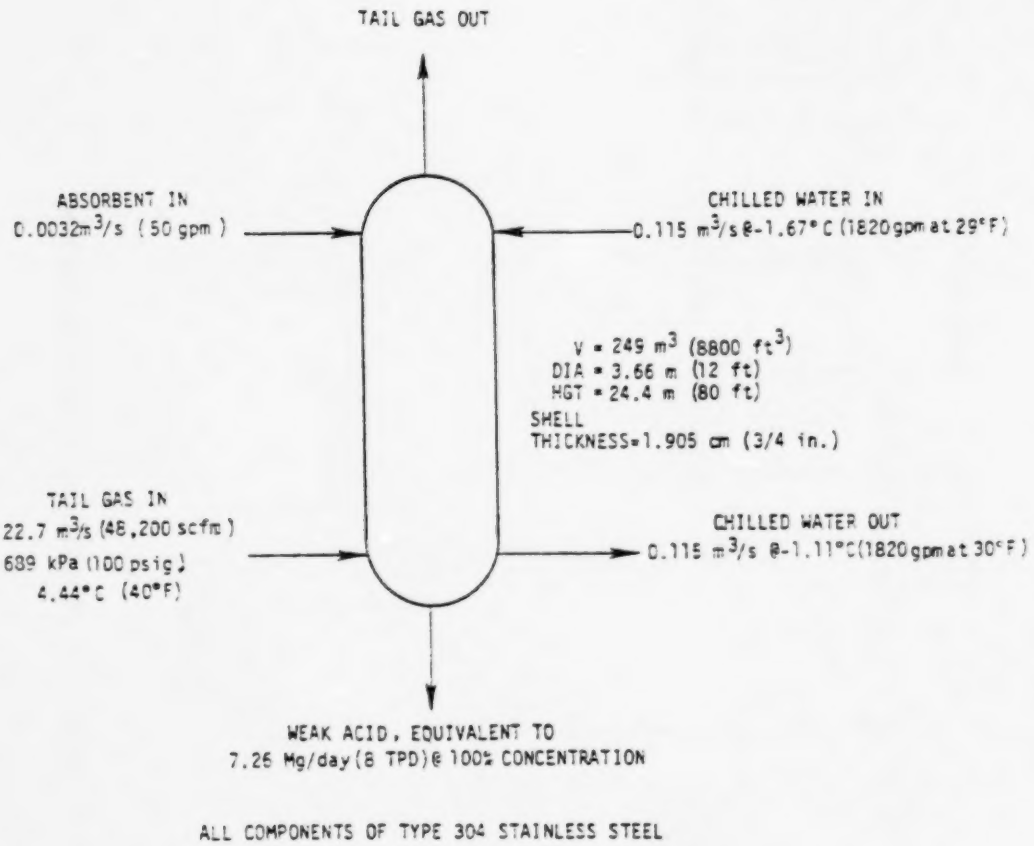
TAIL GAS OUT
ABSORBENT IN
0.0032m3/s (50 gpm)
CHILLED WATER IN
0.115 m3/s @-1.67°C (1820 gpm at 29°F)
V = 249 m3 (8800 ft3)
DIA = 3.66 m (12 ft)
HGT = 24.4 m (80 ft)
SHELL
THICKNESS=1.905 cm (3/4 in.)
TAIL GAS IN
22.7 m3/s (48,200 scfm)
689 kPa (100 psig)
4.44°C (40°F)
CHILLED WATER OUT
0.115 m3/s @-1.11°C (1820 gpm at 30°F)
WEAK ACID, EQUIVALENT TO
7.26 Mg/day (8 TPD) @ 100% CONCENTRATION
ALL COMPONENTS OF TYPE 304 STAINLESS STEEL

Figure 6-1. Secondary absorber tower input and output for a 454 Mg/day (500 TPD) nitric acid plant.

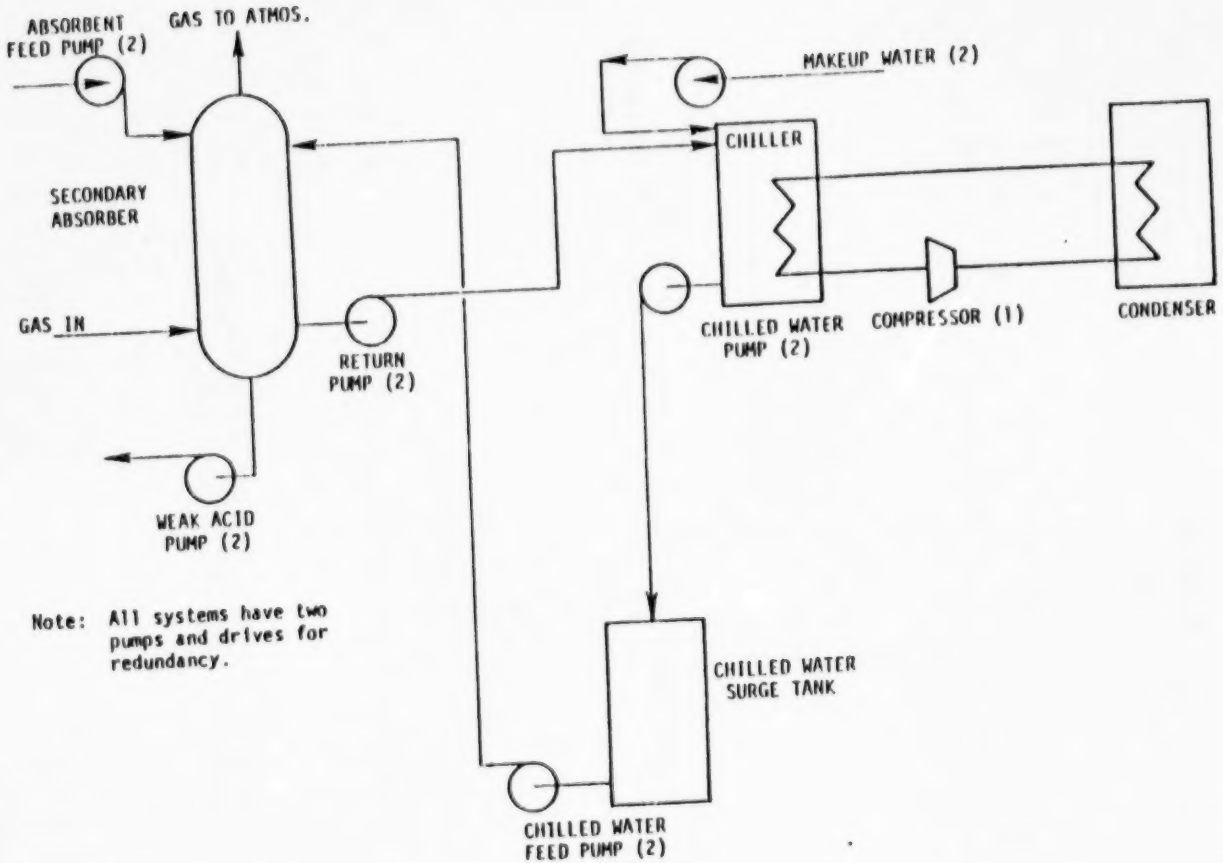

Figure 6-2. Schematic of extended absorption system.

TABLE 6-1. CAPITAL COST SUMMARY FOR AN EXTENDED ABSORPTION SYSTEM [PLANT WITH A CAPACITY OF 181 Mg/day (200 tons/day)] (in January 1983 dollars)

Description	Cost, $1000
A. Direct Costs	
1. Absorber tower[a]	330
2. Pumps and drives[b]	77
3. Chilled water system[c]	20
4. Piping, valves, and fittings[d]	75
5. Electrical[e]	44
6. Instrumentation[f]	44
Total Direct Costs (TDC)	590
B. Indirect Costs	
1. Contractor's fee (6% of TDC)[g]	35
2. Engineering (10% of TDC)[g]	59
3. Construction expense (8% of TDC)[g]	47
Total Indirect Costs (TIC)	141
C. Contingency (10% of TDC and TIC)[g]	73
Total Capital Cost	804

[a] Reference 1, pp. 768, 769, 770, 772.
[b] Reference 1, pp. 555, 557, 558.
[c] Reference 2, pp. 265, 278.
[d] Reference 1, pp. 529, 530.
[e] Reference 1, p. 171.
[f] Reference 1, p. 170.
[g] Reference 1, p. 164.

TABLE 6-2. CAPITAL COST SUMMARY FOR AN EXTENDED ABSORPTION SYSTEM [PLANT WITH A CAPACITY OF 454 Mg/day (500 tons/day)] (in January 1983 dollars)

Description	Cost, $1000
A. Direct Costs	
1. Absorber tower[a]	558
2. Pumps and drives[b]	100
3. Chilled water system[c]	40
4. Piping, valves, and fittings[d]	185
5. Electrical[e]	74
6. Instrumentation[f]	74
Total Direct Costs (TDC)	1031
B. Indirect Costs	
1. Contractor's fee (6% of TDC)[g]	62
2. Engineering (10% of TDC)[g]	103
3. Construction expense (8% of TDC)[g]	82
Total Indirect Costs (TIC)	247
C. Contingency (10% of TDC and TIC)[g]	128
Total Capital Cost	1406

[a] Reference 1, pp. 768, 769, 770, 772.
[b] Reference 1, pp. 555, 557, 558.
[c] Reference 2, pp. 265, 278.
[d] Reference 1, pp. 529, 530.
[e] Reference 1, p. 171.
[f] Reference 1, p. 170.
[g] Reference 1, p. 164.

TABLE 6-3. CAPITAL COST SUMMARY FOR AN EXTENDED ABSORPTION SYSTEM [PLANT WITH A CAPACITY OF 907 Mg/day (1000 tons/day)] (in January 1983 dollars)

Description	Cost, $1000
A. Direct Costs	
1. Absorber tower[a]	818
2. Pumps and drives[b]	191
3. Chilled water system[c]	70
4. Piping, valves, and fittings[d]	292
5. Electrical[e]	109
6. Instrumentation[f]	109
Total Direct Costs (TDC)	1589
B. Indirect Costs	
1. Contractor's fee (6% of TDC)[g]	95
2. Engineering (10% of TDC)[g]	159
3. Construction expense (8% of TDC)[g]	127
Total Indirect Costs (TIC)	381
C. Contingency (10% of TDC and TIC)[g]	197
Total Capital Cost	2167

[a] Reference 1, pp. 768, 769, 770, 772.
[b] Reference 1, pp. 555, 557, 558.
[c] Reference 2, pp. 265, 278.
[d] Reference 1, pp. 529, 530.
[e] Reference 1, p. 171.
[f] Reference 1, p. 170.
[g] Reference 1, p. 164.

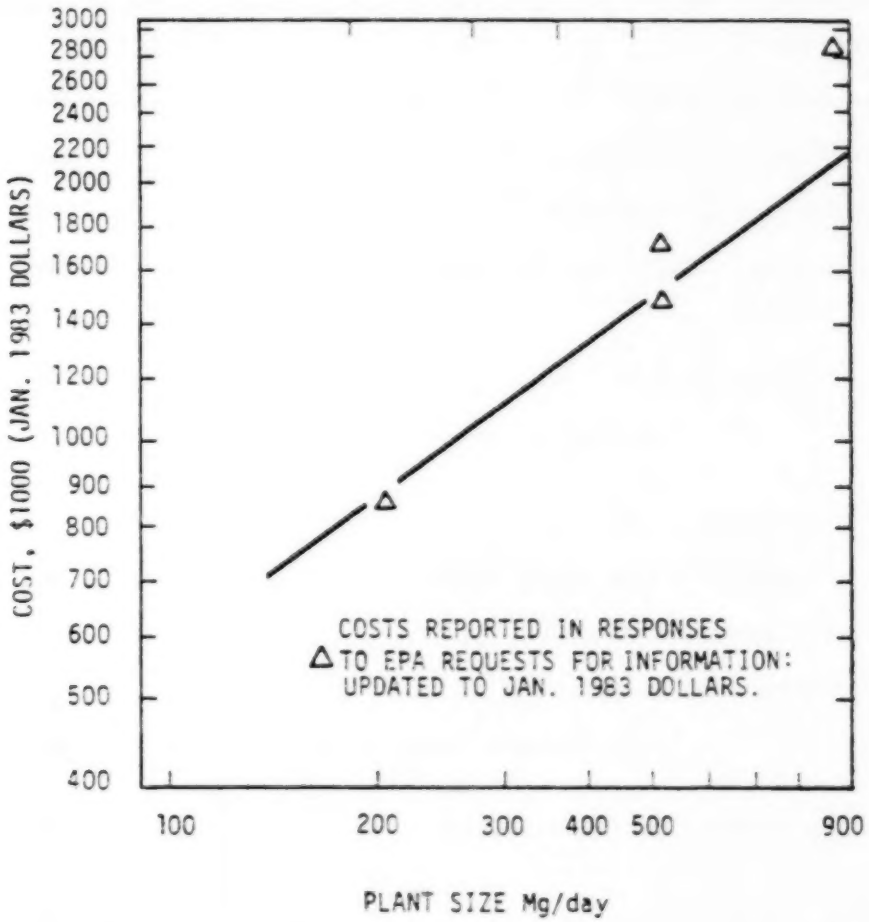

Figure 6-3. Capital cost of extended absorption system for nitric acid plant.

acid recovered varies greatly from plant to plant, and its value is somewhat uncertain. Although nitric acid prices are quoted in the Chemical Marketing Reporter, these prices are not directly applicable because most of the manufacturing plants are captive facilities and hence there is no established market. As shown in Table 6-4, the reported prices do not fluctuate as one would expect of a commodity chemical. The table also shows that the concentration greatly affects the value; the higher grade is currently worth approximately 40 percent more than the lower grade (on a 100 percent nitric acid basis). Thus, although some manufacturers have reported acid credits, there is no correlation between these credits and plant size. For comparison purposes, consider the effect of control efficiencies and acid prices on a 454 Mg/day plant as follows:

Assumed base efficiency, %	Increased efficiency, %	Acid recovered, Mg/yr	Credit, $1000	
			$215/Mg	$308/Mg
98	0	0	0	0
98	1.0	1836	358	514
98	1.2	2204	430	617
98	1.4	2571	501	720
98	1.6	2880	561	806

Since the estimated annualized costs for an extended absorption system on such a plant is about $610,000 (without acid credit), the net annualized cost can range from as much as +$250,000 to -$200,000.

The value of the recovered acid is based on the following assumptions:

(1) Acid production increases by 1.6 percent.

(2) The increased production is a weak acid having a value of $195 per ton.

Tables 6-5 through 6-7 present a breakdown of the annualized cost estimates for each model plant. These estimates define the cost curves shown on Figure 6-4. The annualized cost data reported in the responses to EPA requests for information were not complete enough to be compared

TABLE 6-4. NITRIC ACID PRICES[a]
($/Mg)

Year	Acid Concentration	
	52.3 - 67.2%	94.5 - 98%
1975	127	231
1976	127	231
1977	127	231
1978	127	231-264
1979	193	264
1980	193	264
1981	193	264
1982	215	308

[a] Year-end prices based on data reported by Chemical Marketing Reporter: all prices on 100% nitric acid basis.

TABLE 6-5. ANNUALIZED COST SUMMARY FOR AN EXTENDED ABSORPTION SYSTEM [PLANT WITH A CAPACITY OF 181 Mg/day (200 tons/day)] (in January 1983 dollars)

Cost element	Cost, $1000
A. DIRECT OPERATING COSTS	
1. Utilities	
a. Water ($0.50/1000 gal)	13
b. Electricity ($0.05/kWh)	60
2. Operating Labor	
a. Direct ($15/man-hour)	32
b. Supervision (20% of direct labor)	6
3. Maintenance and Supplies (4% x Capital Cost)	
a. Labor and material	
b. Supplies	32
B. CAPITAL CHARGES	
1. Overhead	
a. Plant (50% x A2 and A3 above)	36
b. Payroll (20% x A2 above)	8
2. Fixed Costs	
a. Capital recovery (13.5% x Capital Cost)	106
b. Insurance, taxes, and G&A (4% x Capital Cost)	32
C. SUBTOTAL	325
D. CREDIT FOR RECOVERED ACID	224
E. NET ANNUALIZED COST	101

TABLE 6-6. ANNUALIZED COST SUMMARY FOR AN EXTENDED ABSORPTION SYSTEM [PLANT WITH A CAPACITY OF 454 Mg/day (500 tons/day)] (in January 1983 dollars)

Cost element	Cost, $1000
A. DIRECT OPERATING COSTS	
1. Utilities	
a. Water ($0.50/1000 gal)	36
b. Electricity ($0.05/kWh)	151
2. Operating Labor	
a. Direct ($15/man-hour)	48
b. Supervision (20% of direct labor)	10
3. Maintenance and Supplies (4% x Capital Cost)	
a. Labor and material	
b. Supplies	56
B. CAPITAL CHARGES	
1. Overhead	
a. Plant (50% x A2 and A3 above)	59
b. Payroll (20% x A2 above)	12
2. Fixed Costs	
a. Capital recovery (13.5% x Capital Cost)	185
b. Insurance, taxes, and G&A (4% x Capital Cost)	56
C. SUBTOTAL	613
D. CREDIT FOR RECOVERED ACID	561
E. NET ANNUALIZED COST	52

TABLE 6-7. ANNUALIZED COST SUMMARY FOR AN EXTENDED ABSORPTION SYSTEM [PLANT WITH A CAPACITY OF 907 Mg/day (1000 tons/day)] (in January 1983 dollars)

Cost element	Cost, $1000
A. DIRECT OPERATING COSTS	
1. Utilities	
a. Water ($0.50/1000 gal)	65
b. Electricity ($0.05/kWh)	325
2. Operating Labor	
a. Direct ($15/man-hour)	65
b. Supervision (20% of direct labor)	13
3. Maintenance and Supplies (4% x Capital Cost)	
a. Labor and material	
b. Supplies	87
B. CAPITAL CHARGES	
1. Overhead	
a. Plant (50% x A2 and A3 above)	85
b. Payroll (20% x A2 above)	16
2. Fixed Costs	
a. Capital recovery (13.5% x Capital Cost)	285
b. Insurance, taxes, and G&A (4% x Capital Cost)	87
C. SUBTOTAL	1028
D. CREDIT FOR RECOVERED ACID	1118
E. NET ANNUALIZED COST	(90)

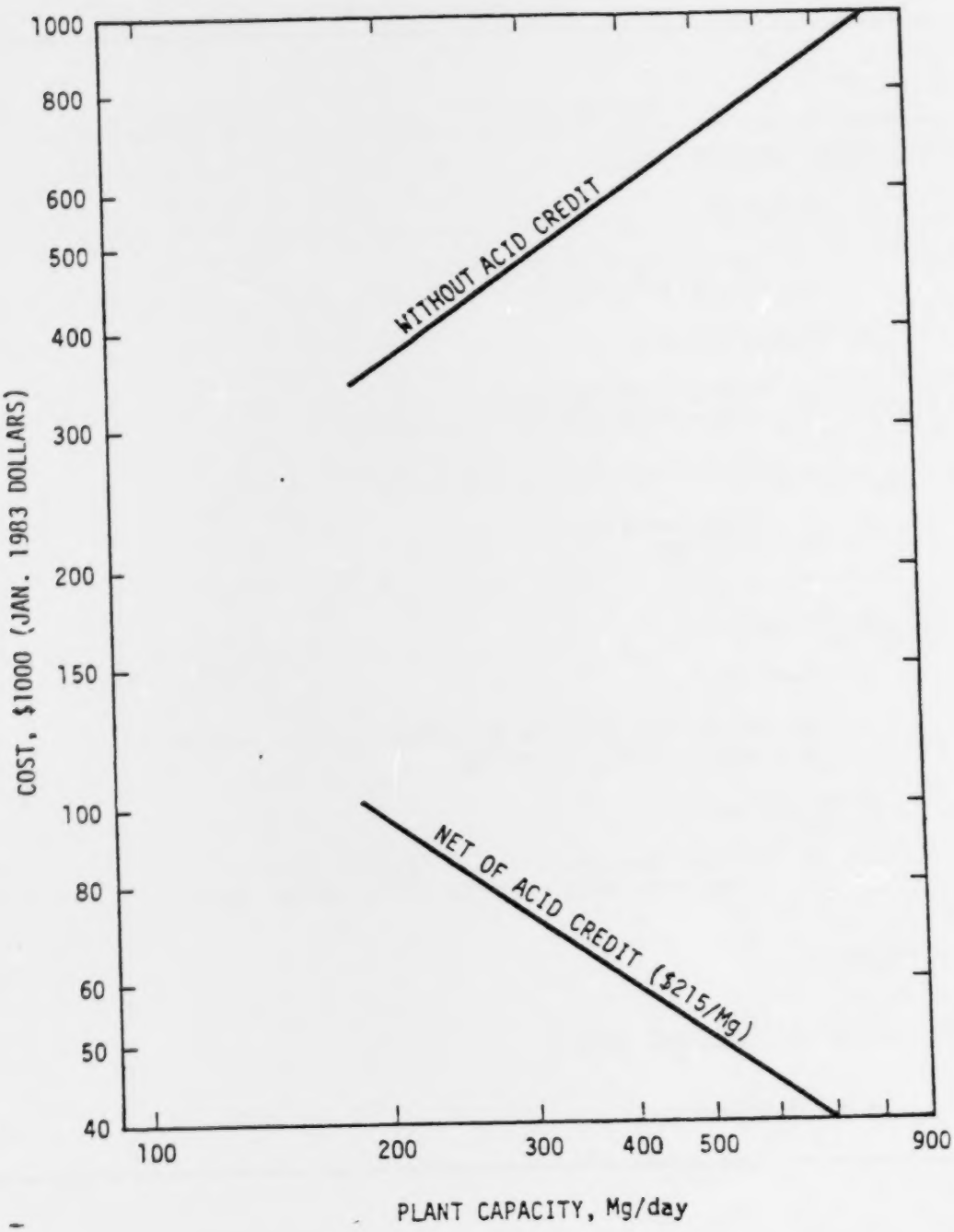

Figure 6-4. Annualized costs of extended absorption system for nitric acid plant.

with the estimated costs. Also, as previously stated, the costs are highly sensitive to the quantity and quality of the recovered acid. The problem of comparing annualized costs is exacerbated further by the scarcity of open-market price data.

6.2 CATALYTIC REDUCTION

6.2.1 Capital Costs

Although nonselective reduction of tail-gas pollutants is generally considered a part of the process (because of the recovery of the heat), it is generally recognized that some portion of the system constitutes air pollution control. For this study, we assume that the catalytic treatment unit, the catalyst, the short run of pipe on either side of the unit for the gases, and the fuel lines are all allocable to pollution control. No public sources of cost information could be found for the catalytic reduction unit. This unit is unlike normal incinerators because of the high pressure (689 kPa) of the inlet gases. Both D. M. Weatherly and a fabricator of such units were contacted; however, because of the proprietary nature of the unit and the lack of specific design specifications, they were unable to provide any cost data. Reportedly, one plant has a unit for which it paid a turnkey price of $2.3 million (actual reported figure updated to January 1983 dollars). This represents the cost of the catalytic unit and the catalyst. The application of this cost to the model plants, by use of the Six-Tenths Power Rule, yields the following capital costs:

Plant capacity, Mg/day	Capital cost, 10^6 (Jan. 1983 dollars)
200	0.94
500	1.63
1000	2.47

6.2.2 Annualized Costs

Direct annualized costs consist of the fuel (natural gas assumed) used in the catalytic reduction unit, operating labor, and maintenance labor and supplies. Effective fuel use is reduced by post-oxidation heat recovery. According to one manufacturer's response to an EPA request for

information, a unit that treats 30.1 m^3/s (64,000 scfm) of tail gas consumes about 1237 m^3 (45,000 ft^3) of natural gas per hour. The heat content of this natural gas is about 45.6 GJ (43 million Btu), of which 23.5 GJ (22.2 million Btu), or 52 percent, is recovered downstream. Thus, the net energy requirement is about 0.00574 GJ (0.00542 million Btu) per 28.3 m^3 (1000 scf) of tail gas. Direct operating labor is estimated at 0.5 man-hour per shift, regardless of the unit size. As with the extended absorption system, maintenance and supplies are estimated at 4.0 percent of the capital cost of the facility. This includes the average cost of catalyst replacement. Reportedly, the catalyst must be replaced every 3 to 8 years at a cost of about $350,000 for a plant producing 816 Mg/day (900 tons/day). Thus, the estimated average annual cost of catalyst replacement at the model plants is:

Plant size, Mg/day	Cost, $1000
181	14
454	36
907	71

Because the catalytic reduction process is less complex than the extended absorption process, one would also expect maintenance costs to be less, but the catalyst replacement costs tend to equalize the overall expense.

Estimates of indirect costs (capital charges) are based on percentage factors similar to those used for the extended absorption system costs. Tables 6-8 through 6-10 present a detailed breakdown of the annualized costs for the three model plants. Note that two items--utilities and capital recovery--account for 70 to 80 percent of the total costs.

6.3 COST EFFECTIVENESS

The cost of controlling NO_x emissions can be related to the quantity of pollutant removed from the exhaust gas stream by using the annualized costs as a basis. Because costs tend to follow the 0.6 Power Rule (so-called "economies of scale"), the cost-effectiveness of the regulation is more attractive to larger plants. The estimated quantity of NO_x controlled by the NSPS requirements is as follows:

TABLE 6-8. ANNUALIZED COST SUMMARY FOR CATALYTIC REDUCTION [MODEL PLANT WITH A CAPACITY OF 181 Mg/day (200 tons/day)] (in January 1983 dollars)

Cost element	Cost, $1000
A. DIRECT OPERATING COSTS	
1. Utilities	
a. Natural gas (net of recovered heat) at $4.00/MBtu	210
2. Operating Labor	
a. Direct ($15/man-hour)	11
b. Supervision (20% x direct labor)	2
3. Maintenance and Supplies (4% x Capital Cost)	
a. Labor and material	
b. Supplies	38
B. CAPITAL CHARGES	
1. Overhead	
a. Plant (50% x A2 and A3 above)	25
b. Payroll (20% x A2 above)	3
2. Fixed Costs	
a. Capital recovery (13.5% x Capital Cost)	124
b. Insurance, taxes, and G&A (4% x Capital Cost)	38
C. TOTAL	451

TABLE 6-9. ANNUALIZED COST SUMMARY FOR CATALYTIC REDUCTION [MODEL PLANT WITH A CAPACITY OF 454 Mg/day (500 tons/day)] (in January 1983 dollars)

Cost element	Cost, $1000
A. DIRECT OPERATING COSTS	
1. Utilities	
a. Natural gas (net of recovered heat) at $ 4.00/MBtu	530
2. Operating Labor	
a. Direct ($15/man-hour)	11
b. Supervision (20% x direct labor)	2
3. Maintenance and Supplies (4% x Capital Cost)	
a. Labor and material	
b. Supplies	65
B. CAPITAL CHARGES	
1. Overhead	
a. Plant (50% x A2 and A3 above)	39
b. Payroll (20% x A2 above)	3
2. Fixed Costs	
a. Capital recovery (13.5% x Capital Cost)	214
b. Insurance, taxes, and G&A (4% x Capital Cost)	65
C. TOTAL	929

TABLE 6-10. ANNUALIZED COST SUMMARY FOR CATALYTIC REDUCTION [MODEL PLANT WITH A CAPACITY OF 907 Mg/day (1000 tons/day)] (in January 1983 dollars)

Cost element	Cost, $1000
A. DIRECT OPERATING COSTS	
1. Utilities	
a. Natural gas (net of recovered heat) at $4.00/MBtu	1050
2. Operating Labor	
a. Direct ($15/man-hour)	11
b. Supervision (20% x direct labor)	2
3. Maintenance and Supplies (4% x Capital Cost)	
a. Labor and material	
b. Supplies	99
3. CAPITAL CHARGES	
1. Overhead	
a. Plant (50% x A2 and A3 above)	56
b. Payroll (20% x A2 above)	3
2. Fixed Costs	
a. Capital recovery (13.5% x Capital Cost)	325
b. Insurance, taxes, and G&A (4% x Capital Cost)	99
C. TOTAL	1645

Plant size, Mg/day	NO_x removed, Mg/yr
181	391
454	977
907	1955

These quantities assume that uncontrolled NO_x emissions are about 0.0075 kg/kg of acid produced (15 lb/ton of acid produced), which is equivalent to an NO_x concentration of 1000 ppm in the exhaust gas. The required reduction to 200 ppm would remove 0.0060 kg/kg (12 lb/ton) of acid produced. The cost effectiveness of each control alternative is shown in Table 6-11. The cost effectiveness of extended absorption ranges from a cost savings of $46 per megagram for a 970 Mg/D plant to a cost of $258 per megagram from a 181 Mg/D plant. For catalytic reduction, the cost effectiveness ranges from $841 per megagram for a 970 Mg/D plant to $1,153 per megagram for a 181 Mg/D plant. Plants with capacities greater than about 650 Mg/day actually benefit financially by using extended absorption because the acid credits exceed the control costs. However, the amount of credit is sensitive to the recovery efficiency at each installation and to the value placed upon the recovered acid. Overall, the cost effectiveness figures are in the reasonable range. Figure 6-5 is a graphical presentation of the cost effectiveness data.

6.4 REFERENCES

1. Peters, M. S., and K. D. Timmerhaus. Plant Design and Economics for Chemical Engineers. 3rd Ed. McGraw-Hill, New York. 1980.

2. Means, R. S. Building Construction Cost Data, 1983.

TABLE 6-11. COST EFFECTIVENESS RATIOS FOR MODEL PLANTS USING EXTENDED ABSORPTION AND CATALYTIC REDUCTION CONTROLS (in January 1983 dollars)

Control Method	Plant Size Mg/day (tons/day)	Annualized Cost ($1000/yr)	NO_x Removed (Mg/yr)	Cost Effectiveness ($/Mg NO_x)
Extended Absorption	181 (200)	101	391	258
Extended Absorption	454 (500)	52	977	53
Extended Absorption	907 (1000)	(90)	1,955	(46)[a]
Catalytic Reduction	181 (200)	451	391	1,153
Catalytic Reduction	454 (500)	929	977	951
Catalytic Reduction	907 (1000)	1,645	1,955	841

[a] Value of product recovered is greater than the control cost, resulting in a saving.